

*The Change of Carbon Disulphide into a Gaseous Product
Condensable and Explosive near the Temperature of Liquid
Air.*

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(Received and Read February 10, 1910.)

In a note communicated to the Society recently we described the preparation and properties of a polymeric form of carbon monosulphide. It was to be expected that carbon monosulphide would be a gas boiling at about -130° C.; yet the interaction of thiophosgene and nickel carbonyl at temperatures as low as -20° C. resulted in the formation of a polymeride, while when the same reaction was tried at -80° C. no change could be observed in the course of several hours.

The decomposition of carbon disulphide by light, studied by Sidot, also produces a polymeric form of carbon monosulphide, and we have shown that when this change is effected at -80° C. by means of ultra-violet light a similar substance is apparently formed.

It seemed possible that carbon disulphide vapour at low pressures might be decomposed under the influence of the silent electric discharge or of the ultra-violet radiation associated with it. The conditions might then be favourable to the stability of the monomolecular carbon monosulphide, provided a rapid current of the hypothetical vapour could be passed through the discharge tube; as the presumably unstable gaseous carbon monosulphide might remain unpolymerised, in the presence of sulphur and a large excess of carbon disulphide vapour, for a sufficient time to allow it to be condensed together with the unchanged carbon disulphide when cooled to the temperature of liquid air.

This anticipation was experimentally examined in the following way. A bulb containing carbon disulphide was sealed on to an annular vessel through which the silent electric discharge could be passed, and the latter was sealed to a U-tube made of quill tubing and a bulb containing charcoal. While the bulb containing carbon disulphide was immersed in liquid air, the rest of the apparatus was thoroughly dried and cleaned by heating and exhausting by means of a good air pump; it was then sealed off and the charcoal bulb cooled in liquid air. The apparatus made solely of glass was now so thoroughly exhausted that no discharge would pass through the "ozoniser." The bulb

containing carbon disulphide was now transferred from liquid air to a paste of solid carbon dioxide and ether, and thus maintained at a temperature of -80°C . In this way a rapid stream of carbon disulphide vapour at a steady pressure of about 1 mm. passed through the "ozoniser" and the U-tube, and was condensed in the charcoal bulb. On cooling the U-tube in liquid air, the carbon disulphide vapour was condensed and solidified as a white crystalline solid ring. When, after five or ten minutes, the U-tube was removed from the liquid air and allowed to rise in temperature, the carbon disulphide melted and quickly evaporated into the charcoal bulb, leaving no residue. The charcoal vacuum was maintained throughout the experiment, in order to ensure the absence of pressure due to any permanent gas.

While the U-tube was cooled in liquid air, the silent discharge was caused to pass through the vapour in the "ozoniser," causing a bluish light to fill the vessel: the discharge could be stopped at once by cooling the carbon disulphide bulb in liquid air. After the discharge had been allowed to pass for five minutes, a faint brown ring was noticed in the U-tube about a centimetre above the level of the surface of the liquid air. The liquid air was then removed, and the temperature of the U-tube allowed to rise, when a flash of light, accompanied by a detonation, was observed, and the surface of the U-tube was found to be partly covered with a dark brown deposit. The detonation was usually gentle, but was sometimes so violent that the tube was shattered. A similar explosion may take place in the charcoal condenser.

When the conditions are arranged so that the temperature gradient in the U-tube is steep, as it is when the vacuum vessel surrounding it is filled to the top with liquid air, then the transformation may take place during the condensation, and no flash will occur when the temperature is allowed to rise. If, on the other hand, the temperature gradient is not steep, as when the vacuum vessel is only half filled with liquid air, the flash can always be observed in a darkened room and frequently also in daylight.

On examination, the interior of the "ozoniser" is found to be partly covered with a thin brownish deposit which consists partly of sulphur and can be dissolved away by carbon disulphide. When the potential of the discharge was increased until sparks passed through the air outside the "ozoniser," then its inside surface became coated with a brown deposit similar in appearance to that which was formed in the U-tube.

In order to show that the brown deposit in the U-tube was due to the change of a gaseous substance, a plug of asbestos or of cotton wool, from 2 to 6 cm. in length, was placed in a wider part of the tube between the "ozoniser" and the U-tube. The flash of light, detonation, and formation of a brown deposit took place in the U-tube as before.

The phenomena as described above were also observed when an "ozoniser" with outside terminals of tinfoil was completely immersed in paraffin oil: this excludes the possibility of ozone being formed in the apparatus through air leakage due to any piercing of the glass by the electric discharge.

The apparatus was slightly modified so that the bulb containing carbon disulphide and also the U-tube could be detached and weighed, so as to obtain a rough estimate of the ratio between the weight of carbon disulphide passed through the "ozoniser" and the weight of the brown solid produced. In a large number of experiments with different forms of "ozoniser," each lasting from 10 to 30 minutes, it was found that the ratio of the weights varied from 9 to 1 to 16 to 1. In each experiment from 20 to 30 milligrammes of carbon disulphide were evaporated.

The properties of the brown deposit formed in the U-tube, in so far as we have been able to examine them with the small amount of material which can be obtained in this way, are almost identical with these of the polymeric form of carbon monosulphide which we have described. The deposit contains carbon and sulphur, is soluble in concentrated sulphuric acid to a brown-purple solution, and in alcoholic caustic soda to a very dark brown solution from which acids precipitate it apparently unchanged.

It would therefore seem fair to conclude that carbon disulphide vapour has been decomposed, by the silent electric discharge, into sulphur and gaseous carbon monosulphide, that the latter has been condensed with the unchanged carbon disulphide at the temperature of liquid air, and that it polymerises at a slightly higher temperature with explosive violence to the brown solid. In any case the experiments seem to suggest the existence of a new volatile sulphide of carbon.

If the above suggestion is correct, then the vapour of carbon disulphide is finally converted into two solids, and its pressure should disappear; but so long as only gaseous carbon monosulphide is formed there should be no change of pressure. An "ozoniser" sealed to a mercury manometer was carefully cleaned by heating under exhaustion and pure dry carbon disulphide vapour was admitted to a pressure of 15 mm., the apparatus sealed and the silent discharge passed through the vapour. In about 15 minutes the pressure had fallen to 1 mm., at which value it remained. This shows that carbon disulphide has been converted into non-volatile products, either sulphur and polymerised carbon monosulphide or the latter along with free carbon.

The influence of heat on the rapidly moving gaseous mixture which came from the "ozoniser" was now examined, and it was found that the gas in the presence of excess of carbon disulphide vapour was surprisingly stable. Some

of the gas was still present after passing the product through a tube immersed in boiling sulphur or even through a short length of red hot tube, but it was completely destroyed after passing through 10 cm. of red hot tube loosely packed with asbestos.

This unexpected stability at high temperatures corresponds with a character of endothermic bodies and suggests that the gas only becomes highly unstable when condensed, and that it might be preserved for some time in the presence of excess of carbon disulphide vapour at low pressures. In order to test this possibility, a litre flask with a delivery tube leading nearly to the bottom was introduced between the "ozoniser" and the U-tube and the apparatus made solely of glass exhausted as before. When the discharge had been passing for about 10 minutes the explosive gas could be detected by the flash got in the usual way in the small U-tube cooled in liquid air. A small portion of the surface of the flask was now cooled by the application of a sponge containing liquid air, when a deposit of solid carbon disulphide was soon formed. On removing the cooling agent this carbon disulphide soon melted to a *coloured* liquid and quickly evaporated, leaving a brown deposit. After a few minutes the flask being again full of gas the charcoal bulb was shut off from the apparatus by means of a tap and the discharge stopped; thus the large flask was left filled with carbon disulphide vapour containing about 10 per cent. of the new gaseous body if assumed to be carbon monosulphide. At different intervals in separate experiments the cooling was repeated and it was found that the deposit of carbon disulphide was coloured and left a residue at any time less than 30 seconds after the discharge had been stopped, but was colourless and left no residue when a minute had elapsed. After several experiments had been made, the general surface of the flask was covered with a visible brown deposit. It therefore appears that the gaseous sulphide of carbon polymerises rapidly at the ordinary temperature, even at low pressures and in the presence of a large excess of carbon disulphide. It may be possible to separate the new body from the admixed carbon disulphide by fractional distillation at very low temperatures. We hope to continue this investigation and to extend a similar study to other bodies.
